Fe-$3s$ core-level splitting and local magnetism in Fe$_2$VAl

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X-ray and soft x-ray photoelectron spectra were taken on Fe$_2$VAl samples. The Fe-$3s$ spectra show a shoulder on the higher binding energy side of the main peak, split by ≈ 4.7 eV. Based on current understanding of core-level multiplet splitting in transition-metal compounds, we believe this is direct evidence of a local moment in Fe$_2$VAl.

I. INTRODUCTION

Fe$_2$VAl was shown recently to have fascinating physical properties.[1] With an enhanced density of states at E_F seen in photoemission and specific-heat measurements, and the negative temperature coefficient of its unusually large resistivity, heavy fermion physics was proposed. There is also evidence contradictory to the ground state of a Kondo lattice. First, $3d$ electrons are more delocalized than their $4f$ counterparts. Significant overlap of the wave functions tends to suppress the Kondo effect, making $3d$ heavy fermions very rare. Two candidates are FeSi (Ref. 2) and LiV$_2$O$_4$.[3] Second, there is experimental evidence of superparamagnetism in this material, from results of Mössbauer,[4] magnetic-field-dependent specific heat,[5] and saturation magnetization experiments.[4,6] *Ab initio* calculations,[7–10] assuming V, Fe, Al, and Fe occupy diagonal sites sequentially in a Heusler structure, gave a *nonmagnetic* ground state with semimetallic band structure. Although most of the theoretical speculations agreed on spin fluctuations as the primary cause of those unusual properties of Fe$_2$VAl,[7,8] not much quantitative understanding was possible because of the lack of experimental data, particularly regarding the magnetic state of this alloy. There were also theoretical speculations that dynamic exciton correlations, which have nothing to do with magnetism, might be responsible for the anomalous physical properties of Fe$_2$VAl.[9] The valence band of Fe$_2$VAl has since been studied by resonant photoemission spectroscopy.[11] The partial densities of states found agree very well with those from band-structure calculations, except near the Fermi level. Understanding the magnetism in the ground state is crucial in revealing the physics behind Fe$_2$VAl.

To comprehend the magnetic structure of Fe$_2$VAl, we investigated the Fe core-level multiplet splitting by x-ray photoelectron spectroscopy (XPS). The shallow-core-level multiplet splitting due to local magnetic moments was first observed in mostly ionic $3d$ transition metal compounds.[12,13] In the simplest model, this splitting is due to intra-atomic exchange interaction between unpaired $3d$ electrons and the $3s$ photohole in the final state of the system.[14] Van Vleck's theorem predicts a doublet with separation $\Delta E = (2S + 1)G^2(3s,3d)/5$, with $G^2(3s,3d)$ the $3s-3d$ exchange integral, and S the ground-state spin. The intensity ratio in this model is proportional to the ratio of angular momentum multiplicity, $S/(S+1)$. Correlation of the size of the splitting

of the $3s$ orbital and the hyperfine field was soon realized in some compounds containing Fe or Mn.[15] Based on these findings, $3s$ multiplet splitting started to be used as a diagnostic tool for local moments.[16] However, calculations using Hartree-Fock theory, based on the one-electron approximation, yielded too large a splitting and a different intensity ratio, compared to experiments. Bagus, Freeman, and Sasaki[17] were the first to realize that intra-atomic configuration interaction of the electrons within the same subshell, largely due to the near degeneracy of the orbital energies of the $3p^2$ and $3s3d$ configurations, causes a significant modification to the final states. By including additional internal configurations, they were able to account for both the size of the $3s$ splitting and the intensity ratio of the Mn^{2+} compounds. Their prediction of weaker satellite peaks was later verified by experiments.[18] Furthermore, XPS spectra of gaseous Mn and solid-state Mn^{2+} ionic compounds were compared.[19] No significant difference was found between them, which further affirms the atomic character of these multiplets. Screening due to charge transfer from ligands was not necessary to produce these multiplets.

The success in understanding Mn^{2+} multiplet splittings lies in the half-filled $3d$ shell. Local screening is suppressed due to a large ligand-to-$3d$ charge-transfer gap. Aside from magnetic insulators with Mn^{2+}, however, the relation between $3s$ splitting and the local magnetic moment is not as straightforward. Studies[20,21] have found that for many metals, metalloids, and nonmetals containing Fe, the splitting of $3s$ levels is not proportional to the local moment measured by neutron scattering, saturation magnetization, or hyperfine fields. In two references,[22,23] the Anderson Hamiltonian in the impurity approximation was solved, treating exchange splitting, intra-atomic degeneracy, and screening by ligands on an equal footing. In both accounts, screening was found to be an integral part of XPS spectra. With increasing atomic number of cations (from Mn) or decreasing electronegativity of ligands, the charge-transfer energy from ligand to $3d$ atom becomes smaller; thereby local screening by the charge-transferred $3d$ electron becomes more likely. A direct extraction of exchange energy from the splitting of the two strongest peaks, without regard to local screening, is unwarranted. Experimentally, if the charge-transfer satellite of the $2p$ core level is small, the major multiplet splitting of $3s$ is still a good measure of the exchange energy,[22] with the intrashell
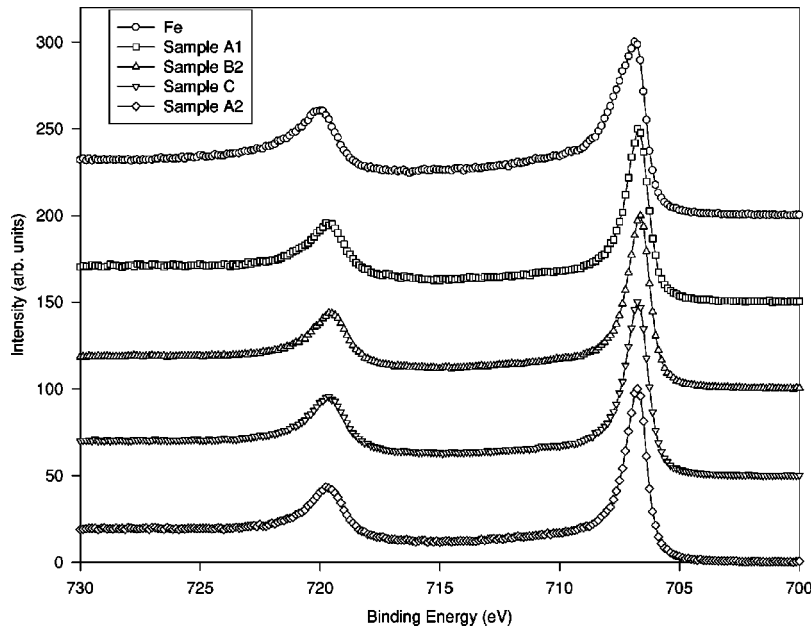
FIG. 1. Experimental Fe-$2p$ spectra. Photon energy is 1487 eV.

redistribution of electrons only contributing to satellites at much higher energy.[18,24]

Recent advances in high-resolution spin-polarized photoemission have made more detailed experiments possible. In separate efforts, three groups[25–27] have measured the $3s$ splitting of Fe metal. One single peak dominates minority-spin emission at the lower binding energy but two structures were discovered in the majority-spin emission 0.9 and 4.5 eV higher in binding energy. Although the theoretical modeling[28] of Fe, based on the atomic Fe $3d^7$ ion, gave a fair estimate of the energy separation of the high- and low-spin final states and also the relative intensities, the origin of the 0.9-eV difference between majority and minority emissions of the high-spin component is still elusive. It is prudent to say that within current understanding, exchange splitting is the cause of the satellite of Fe-$3s$ core level, 4.5 eV below the main peak.

In this work we report the observation of Fe-$3s$ satellite structures in the Heusler-like alloy Fe_2VAl. In conjunction with recent understanding of the multiplet splitting, we propose that this final-state structure is the first signature of local magnetic moments in Fe_2VAl.

II. EXPERIMENTS

The samples involved were grown by the Bridgman method (sample $\mathcal{B}2$), Czochralski method (sample $\mathcal{C}$), and arc melting (samples $\mathcal{A}1$ and $\mathcal{A}2$). Their growth procedure, chemical composition, crystal structure, and magnetic and transport properties were described in another paper.[6] It suffices to point out here that most samples are close to stoichiometric Fe_2VAl with various degrees of Fe and Al deficiency, except for $\mathcal{C}$, which is Fe rich. Severe antisite structural disorder was found in all samples by x-ray diffraction. Saturation magnetization measurements at 2 K found at least two kinds of superparamagnetic clusters in samples $\mathcal{A}2$ and $\mathcal{B}2$. $\mathcal{A}1$ and $\mathcal{C}$ were found to have magnetic transitions

around 18 K and 50 K, respectively.

The XPS spectra at room temperature were taken using a Physical-Electronics 5500 Multi-Technique system with monochromatized Al K_α radiation. A hemispherical electron energy analyzer was used. The resolution of the spectrometer (FWHM) was 0.65 eV, with a spot size around 1 mm $\times 1$ mm. The base pressure of the XPS system was less than 7×10^{-10} Torr, and 4×10^{-10} Torr in the preparation chamber. We have also taken spectra using 150-eV synchrotron radiation at the Synchrotron Radiation Center. With a slit width of 70 μm on a 2-m ERG monochromator and pass energy of the electron analyzer of 50 eV, a comparable resolution was achieved at the Ames-Montana beamline. Pressure of this UHV system is 5×10^{-11} Torr.

The XPS data-analysis package was used to obtain the atomic concentrations. Corrections due to the photoionization cross section of atomic shells, electron escape depth, transmission function of the electron analyzer, and detection angle had been applied. The atomic percentage, obtained by integrating C-$1s$, O-$1s$, Al-$2p$, V-$2p$, and Fe-$2p$ photoelectrons.

Fracturing the samples *in situ* is found to yield surfaces with least oxygen and carbon content. Using inert gas etching or *in-situ* grinding to clean sample surfaces were not proper procedures. During argon-ion bombardment preferential sputtering of the lightest element (Al) was observed. After grinding with a diamond wheel several times, large amounts of oxide and carbon remained on the surface. We chose to break the samples *in situ*. There was always 5 at. % oxygen contamination right after fresh surfaces of Fe_2VAl were uncovered. When these surfaces were further exposed to oxygen, aluminum oxide quickly formed to become the major oxide on the surface. Even with vacuum as good as 5×10^{-11} Torr, aluminum oxide showed up as a distinct shoulder in the Al-$2p$ spectrum 24 h after cleavage. Intensive argon-ion sputtering of the fractured surface of sample $\mathcal{A}2$ yielded about 3 at. % oxygen remaining. Fe and V oxide formation as evidenced by the change of slope at the higher-
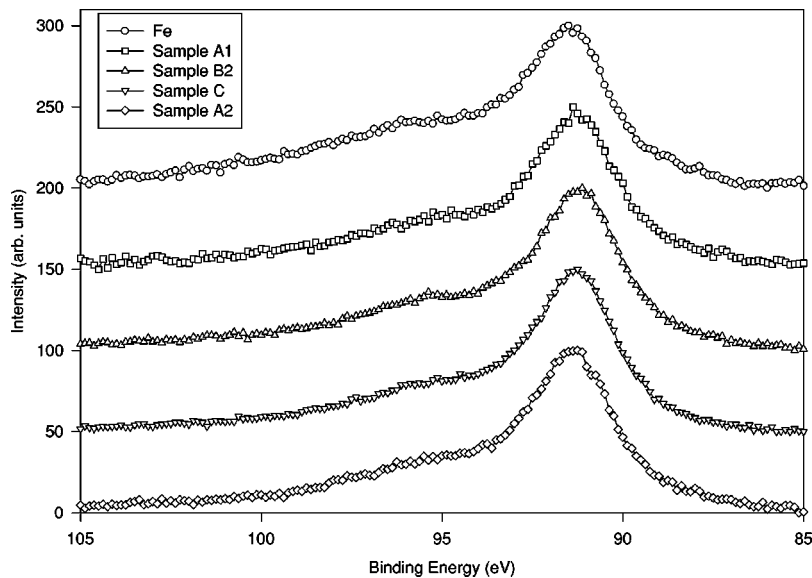
FIG. 2. Experimental Fe-3s spectra. Photon energy is 1487 eV.

binding energy side of the $2p$ peaks were less obvious and were detected only after aluminum oxide peaks were evident. Surface carbon content right after cleaving was less than 4 at. % for all samples except $\mathcal{A}2$, which had almost 9 at. %. We found regularly two peaks associated with the carbon $1s$ orbital. The one with binding energy near 285 eV changed with surface conditions. Associated with the C–H bond, this peak diminished to zero with sputtering but regained its intensity after time in vacuum. The other peak at 283-eV binding energy was identified to be from carbide bonding. This carbide peak gained some intensity in the middle of the sputtering, similar to the carbide formation on the TiFe surface activated by ion bombardment.[29] Terminal carbon intensity in sample $\mathcal{A}2$ is around 3 at. %. Carbon concentration at this level was found to bear no relation to the core-level spectra of any other element. Still, the carbon and aluminum (oxide)

peaks were checked during the integration of the Fe-$2p$ and Fe-$3s$ data to insure that there was no detectable contamination. All spectra discussed in the following were taken right after cleavage, without sputtering and before aluminum oxide appeared. The composition of Fe, V, and Al on these surfaces was compared to the stoichiometries measured by atomic emission spectroscopy.[6] The relative atomic ratios are consistent with each other. Therefore, the electronic and magnetic properties of the *in-situ* fractured surfaces are regarded to be representative of the bulk.

III. RESULTS AND DISCUSSION

Fe-$2p$ and Fe-$3s$ spectra of all Fe$_2$VAl samples, together with that of pure Fe, are shown in Figs. 1 and 2. The Fe-$3p$ spectrum of sample $\mathcal{A}2$ was taken at 150-eV photon energy with better vacuum, and that of pure Fe was taken
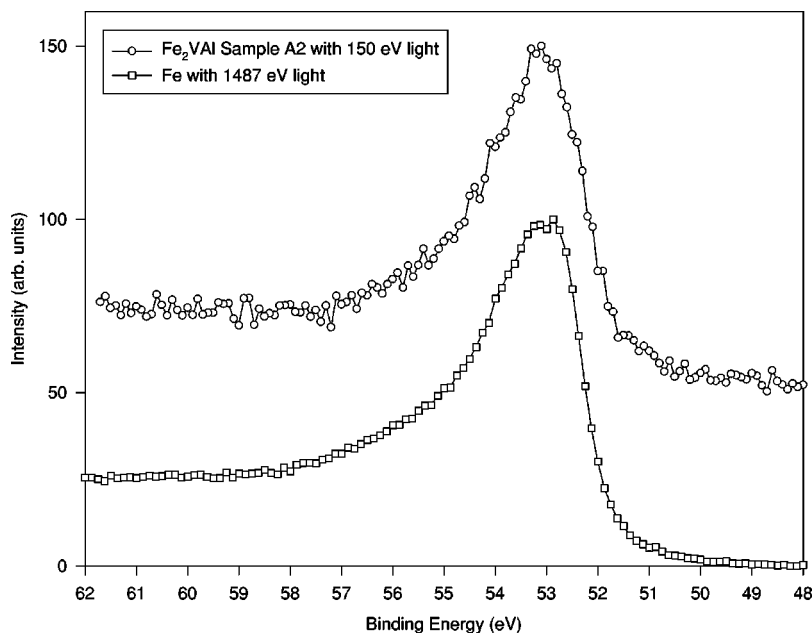

FIG. 3. Experimental Fe-3p spectra.

TABLE I. Comparison of line-shape parameters of Fe-3s spectra and magnetic moments in Fe_2VAl and pure Fe. γ_1 and γ_2 are the Lorentzian widths of the main and satellite peaks. α_1 is the asymmetry parameter of the DS line shape of the main peak. $\alpha_2 \approx 0$ in all fittings. I_1/I_2 is ratio of integrated intensities. μ is the saturation moment measured at 2 K.

Sample	ΔE (eV)	γ_1 (eV)	γ_2 (eV)	α_1	I_1/I_2	$\mu(\mu_B/\text{f.u.})$
σ^a	0.2	0.02	0.2	0.01		
$\mathcal{B}2$	4.7	1.27	2.0	0.13	5.4	0.05
$\mathcal{C}$	4.7	1.23	2.3	0.13	5.4	0.33
$\mathcal{A}1$	4.6	1.27 ± 0.03	2.3 ± 0.3	0.10 ± 0.02	4.1	0.37
$\mathcal{A}2$	4.6	1.25	2.3	0.13	5.1	0.02
Fe	4.9 ± 0.3	1.20 ± 0.03	3.4 ± 0.3	0.15 ± 0.02	2.3	2.2
Fe[30b]	4.8			0.19	3.0	2.2
Fe[20c]	4.9	1.1	1.3-1.8	0.27	4.5	2.2

[a]Standard deviation of our fitting, unless otherwise indicated.
[b]Mg K_α used; linear background subtraction; $\alpha_2 = 0.08$.
[c]$\alpha_1 = \alpha_2$ forced; no background corrections.

with Al $K\alpha$ excitation. They are shown in Fig. 3. All spectra have been normalized to a peak intensity of 100 and displaced relatively for ease of viewing. With only one spin-orbit doublet, none of the Fe-2p spectra has extra peaks due to chemical shifts or plasmon excitations. Without any satellite structure in the 2p or 3p spectra, we can also rule out the importance of local screening. The lesser asymmetry of Fe_2VAl peaks, relative to that of Fe, observed in all core levels hints at the suppressed electron-hole pair excitations near E_F in Fe_2VAl samples. All 3s spectra have shouders around 5 eV below the main peak.

In the case of Fe, spin-polarized photoemission[25–27] reveals the existence of three peaks. With our experimental resolution comparable to the smallest separation of these peaks, we cannot fit all three peaks and perform line-shape analysis. However, we can still compare Fe_2VAl with Fe, in the spirit of Refs. 20 and 30. For each 3s spectrum, a Shirley background[31] was subtracted first and the remainder was fit with two peaks of Doniach-Šunjić (DS) line-shape.[32] The standard deviations of each parameter were obtained in the least-square Marquardt-Levenberg fitting. Relevant parameters of this fitting and selected literature results are given in Table I. The difference between our fitting results and those of Ref. 20 for pure Fe is primarily due to the Shirley background subtraction and the independence of α_1 and α_2 in our fitting. Although the asymmetry parameter α depends on the shape of the density of states near E_F and would allow us to obtain more information,[32] it was recognized that the interference of the nearby majority-spin emission alters the apparent α of the main peak.[26] I_1/I_2 is strongly affected also.

As shown in Table I, all Fe-3s splitting parameters are very similar, although the saturation moment varies by an order of magnitude. All samples show a secondary peak with considerable intensity 4.7 eV below the main peak. This is very similar to the case of pure Fe. Assuming the proportionality of exchange splitting and $2S+1$ still applies, this sec-

ondary peak provides evidence that a large fraction of the Fe atoms in Fe_2VAl carry a local moment of around $2.2\mu_B$. Singh and Mazin[8] found that although Fe_2VAl in the ordered $L2_1$ phase will have no moment on the Fe atoms, the local moment on antisite Fe atoms is very robust, always $2.2–2.3\mu_B$. These XPS spectra therefore confirm the large amount of antisite structural disorder found in Fe_2VAl.[6] The small saturation moments at low temperature do not necessarily contradict the large relative intensity of the satellite. Our study of Fe_2VAl (Ref. 6) has found not only two types of superparamagnetic clusters composed of magnetic antisite Fe atoms, but more antisite Fe atoms that are probably locked in a spin-glass state. The Fe atoms in superparamagnetic clusters give a small saturation moment of $0.02–0.37\mu_B/\text{f.u.}$ at 2 K, probably even less at elevated temperatures. However, all antisite Fe atoms, including those in the spin-glass state, should carry a local moment and contribute to the intensity of the satellite.

In summary, our Fe-3s spectra show that a large number of Fe atoms in Fe_2VAl are in antisite disorder. Each one carries a moment of $2.2\mu_B$. Further spin-polarized photoelectron experiments should clarify the details.

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